Preface

For every phenomenon found in inorganic materials, organic counterparts have been found in the last 50 years. The discovery of metallic conductivity in the inorganic conjugated polymer $(SN)_x$ was a forerunner to the discovery of metallic conductivity in Polyacetylene [1]. It was soon followed by the development of Polypyrrole and Polythiophene, and by the rediscovery of Polyaniline as a conducting polymer [2].

In polymers like Polyacetylene and Polythiophene, doping is by a redox reaction where the incorporation of electron withdrawing groups creates charge carriers in the polymer backbone. In contrast to these polymers, the main doping mechanism in Polyaniline is protonation, that is the attachment of a proton (donated by an acid) to specific sites (imine and amine groups) in the polymer. The protonated groups are also the sites where water and oxygen interact with the charge carriers on the polymer chain.

A wide variety of quasi-particle states (excitons, bipolarons, separated polarons and polaron lattice forms) exist in Polyaniline, in its different states of oxidation and protonation. All of them have different transport and optical signatures. Out of these, only the polaron lattice gives rise to a half-filled conduction band, and therefore a metallic state [3]. This fascinating interplay of protonation and metallic features in Polyaniline, combined with its easy processibility, has made Polyaniline an attractive conducting polymer. Therefore the main focus of this thesis is on the role of the dopant on the electronic and optical properties of doped Polyaniline. The first chapter describes the main features of Polyaniline and its doping by protonation. The second chapter describes the experimental and simulation methods used in this thesis.

Steady improvements in processing have led to reduced disorder in the samples, and have given rise to stronger metallic features like metallic (Drude-like) reflectivity in the infrared frequencies, and a positive temperature coefficient of the logarithmic derivative of the conductivity. High molecular weight Polyaniline doped with sulfonic acid dopants by surfactant-counterion processing, like Polyaniline doped with AMPSA (2-acrylamido-2-methyl-1-propanesulfonic acid) [4] and cast from dichloroacetic acid (DCA), shows all

the metallic features indicative of an intrinsic metallic state [5]. In this thesis, the third chapter describes the spin-charge dynamics of Polyaniline doped with AMPSA (PANI-AMPSA) through X-band Electron Spin Resonance studies [6].

Electron Spin Resonance (ESR) is an important technique to probe the spin-charge dynamics of conducting polymers [7, 8]. The X-band ESR spectra of PANI doped with AMPSA showed the presence of two lines (one broad and one narrow) at all temperatures and doping levels, indicative of two types of spin carriers. Three interesting features were observed in our study: a large linewidth ($\sim$ 100 Gauss), a maximum of ESR linewidth at $\sim$ 25 K, and a surprising independence of linewidth on water/O_2. The temperature dependence of both linewidths suggests that the broad line is due to the delocalised charge carriers in well-ordered regions, and that the narrow line is due to localised spins in the disordered regions in the sample. Although the XRD spectra showed minimal crystallinity, the ESR and SQUID susceptibility had a strong Pauli contribution, indicative of an intrinsic metallic state. A similarity of the temperature dependence of linewidths of PANI-AMPSA with MWNT-s and HOPG graphite suggested that some quasi-2-D (Q2D) ordering is present in PANI-AMPSA.

From Semi-empirical molecular modelling studies, a plausible hydrogen bonding pattern is suggested that can give rise to the Q2D graphene-like arrangement of the PANI polymer chains. This ordering is due to hydrogen bonding between the acrylamido group of the dopant and the amine fragment of the Polyaniline backbone. Hydrogen bonds are not just structural linkers between adjacent chains; they can have subtle effects on electronic states of the polymer backbone due to charge transfer/withdrawal by the hydrogen bond from the delocalised π-electron system of the backbone. The same Q2D model is used to explain the water/oxygen independence of linewidth in PANI-AMPSA.

The temperature dependence of linewidth of both lines has been explained in terms of the QTDG (Quasi Two Dimensional Graphite) model, where a strong exchange interaction is presumed to arise between the 2D delocalised charge carriers and the localised spins, leading to a low-temperature peak in the the linewidth.

Water is known to significantly enhance the conductive properties of doped Polyaniline [9]. A detailed DFT (Density Functional Theory) modelling study of the influence of water in doped Polyanilines is presented, which clearly indicated that water enhances the charge transfer between the counterion and the polymer backbone. The torsion angles between the adjacent phenyl rings of the emeraldine base decrease when the imine nitrogens are protonated by inorganic acids like HCl and HBr, and hydration of the acid counterions

further decrease the torsion angles. In contrast, the torsion angles of the AMPSA protonated Polyaniline are already low (comparable to the hydrated cases), and the charge transferred by AMPSA is also enhanced. Visualisation of the molecular structure of the PANI-AMPSA complex suggested that water molecules may play a minimal role in the electronic properties of AMPSA doped Polyaniline. We suggest the Q2D ordering as the reason for the temperature dependence of the linewidth, the lack of oxygen and water dependence of the linewidth, as well as the enhanced metallic properties in PANI-AMPSA, as compared to other doped Polyanilines.

The electronic states of Polyaniline are modified by both redox processes and protonation. This gives rise to a wide variety of optical states, which can be easily accessed by both applied potential and pH [10]. Therefore Polyaniline displays strong electrochromism across the visible, near-IR (NIR), IR and even microwave spectral regions. This feature has wide applications in electrochromic devices. However, a fundamental understanding of the phenomena behind this electrochromism, the charge carrier(s) responsible, and the relation of nanoscopic morphology and electrochemical properties to the electrochromism, is still not clear.

In the fourth chapter, we have analysed extensive data from electrochromic devices [11]. Clear assignments are that certain population states contribute predominantly to certain spectral regions (e.g. bipolaron states to the IR, the valence band to the visible and other mid-gap states to the microwave). Among more specific findings, a prominent 7μm (0.16 eV) peak in MIR devices is ascribed to bipolarons, while a low-energy transition at 0.054 eV is ascribed to inter/intra-chain transitions. Each of these transitions is tracked with respect to changes in applied potential, as well as correlated with device morphology and construction. Our analysis of UV-Vis-MIR-FIR-microwave results along with detailed SEM data clearly relates performance in different wavelength regions to morphology. Preliminary kinetics analysis show that the diffusion rates in these devices could be improved further. These findings point to the potential design of very broad-band electrochromic systems encompassing the visible through microwave regions.

Polyaniline in its insulating states can be considered as a series of linked oligoanilines. These oligoaniline states can either be considered as a model for describing the properties of the polymer, or can be interesting systems themselves in the light of single-molecular electronic devices [12]. Both applied potential and pH can change the electronic states of these systems. The ability of pH to modify the oxidation states in these systems (and induce electronic transport), and the influence of water on these properties can be a

model for biological systems too. While a wealth of information on oligoanilines has been generated from experiments, computational modelling of these systems is less reported.

Among many computational methods that have been developed for calculation of optical absorption spectra of molecules, Time Dependent Density Functional Theory (TDDFT) is the method with the widest use. TDDFT obtains the excitation energies of a molecule from the linear response of the electronic density to a external perturbing field [13]. Solvent effects, which are known to affect the excitation energies, are included through the SCRF/PCM (Self-consistent Reaction Field/ Polarizable Continuum Model). PCM is a method that treats the solvent molecules as a continuum, and self-consistently evaluates their electronic distribution around the solute.

In the fifth chapter, a systematic study of the optical properties of neutral oligoaniline, in three oxidation states, is performed by varying the chain length and linearity of the backbone. The intrinsic accuracy in the excitation energies obtainable by the *combined* TDDFT/PCM formalism has enabled us to suggest effective oligomer lengths for the optical transitions in Polyaniline; these are 4 rings for emeraldine base, 4–8 rings for leucoemeraldine base and 4 rings for pernigraniline. The sensitivity of the 2.0 eV exciton peak in emeraldine base to the chemical environment is also apparent from this work. The Valence Density of States (VDOS) and vibrational frequencies, that have been obtained in course of these simulations, have been quantitatively analysed and are a useful addition to understanding the optical properties of neutral Polyanilines.

A summary of the results of the dopant and water dependence on the electronic and structural properties of protonated oligoanilines was presented in the third chapter; the appendix describes the methodology in detail. It is worthwhile to emphasize that doped Polyaniline is a system where protonation, hydration and extended π-conjugation all occur together synergistically, and a good overall description of this system is necessary.

Modelling the doped state of Polyaniline is a bit more difficult, due to spin polarisation. Ideally, conducting Polyaniline should be modelled in the solid state, with neighbouring chains, counterions and water molecules. Water is known to reversibly increase the macroscopic conductivity and ESR linewidth of doped Polyaniline. In the sixth chapter of this thesis, optical spectra of the bipolaron, separated polaron, and the polaron lattice forms of doped Polyaniline, explicitly including the counterions (Cl, Br, AMPSA) are obtained by the TDDFT method.

All the polaronic lattice forms show a dominant absorption at 1.0–1.2 eV, with no absorptions in the range 1.4–2.0 eV. The inclusion of water molecules to solvate the

counterions is shown to only weakly modify the optical properties in the polaron lattice form. In the case of polarons on a twisted chain, the 1.0 eV peak is shifted to 1.5 eV. For bipolarons, there is an absorption at 1.3–1.5 eV, along with another peak at 1.8 eV.

Comparing with experimental spectra we suggest that the 1.5, 2.8 eV set belongs to a polaron lattice form wherein the chains are twisted. However, individually the 1.5 eV peak may equally come from bipolarons or separated polarons. The peak at 1.8 eV may either be ascribed to a bipolaron form (in which case there should be a 1.5 eV peak too), or to an isolated polaron. The isolated polaron may also show a peak at 2 eV and 3.5 eV that is clearly from a residual emeraldine base electronic state.

The steady evolution of the (a) 2 eV exciton peak in emeraldine base to a (b) 1.6–1.8 eV peak (isolated polarons) to a (c) 1.5 eV peak in the bipolaron form to (d) 1.3 eV peak in the separated polaron form to (e) a 1.0–1.2 eV peak in the fully doped metallic polaron lattice form is clear. This steady evolution observed from TDDFT simulations may help in clarifying the experimental assignments, especially in electrochemical studies on Polyaniline.

Simulations including the water molecules were performed to study the experimentally observed dramatic changes on hydration in Polyaniline. However hydration of ions is a dynamic process and static geometries may not provide a fully realistic description. Combined *ab initio* Molecular Dynamics (AIMD) and TDDFT calculations may be necessary to realistically model the transport properties of doped Polyaniline. This chapter tries to lay a foundation for such work.

The main results obtained in this thesis are summarized in the conclusion. To conclude, this thesis is on the electronic and optical properties of Polyaniline. An ESR study on AMPSA doped Polyaniline indicated a unique 2D nanoscopic morphology, and this structure was validated by molecular modelling. The detailed analyses on electrochromic devices led us to perform TDDFT simulations of neutral and doped Polyanilines. These simulations have resulted in clear UV-VIS-IR assignments in all forms of Polyaniline.